Growth of device quality amorphous SiGe:H alloys with high deposition rate under helium dilution

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Highly photoconductive amorphous silicon-germanium alloy (a-SiGe:H) films have been developed by plasma-enhanced chemical-vapor deposition using helium dilution (HeD) of the process gases (silane and germane). On comparison with high-quality a-SiGe:H alloys prepared under hydrogen dilution it has been observed that HeD films have higher deposition rates as well as higher mobility lifetime products $\eta\mu\tau$ throughout the alloy range; however, midgap defect densities and Urbach energy values of the two types of materials are nearly the same. Improvement in $\eta\mu\tau$ values of HeD films are found to be consistent with the reduction of microstructural defects in the films. Device potential of the helium-diluted a-SiGe:H films has also been investigated. © *1994 American Institute of Physics.*

I. INTRODUCTION

The development of a high-quality amorphous silicon-germanium (a-SiGe:H) alloy with a low band gap (1.4–1.5 eV) is at present one of the key issues for the enhancement of the stabilized efficiency of multijunction amorphous silicon solar cells.[1] To achieve this goal different deposition methods[2-5] and different combinations of source and diluent gases have been used.[6-8] Until now device quality a-SiGe:H films have been produced by hydrogen dilution (HD) of the source gases (silane and germane).[9,10]

One of the drawbacks of this method is the comparatively low deposition rate which stands in the way of achieving high throughput in the production line. Generally an increase in chamber pressure and/or rf power density is effective in increasing the deposition rate R_D. It has been observed that increases in pressure and power deteriorate the quality of the film. This is due to the increase in the number density of XH_2, XH_2^+, and XH_2^- (X=Si,Ge) types of species which produce a di/polyhydride-dominated network structure in the film.[11]

However, if the helium is used as diluent (HeD) instead of hydrogen under high power and pressure, most of the rf power is consumed by helium itself for the excitation to higher states. This prevents the formation of XH_2 types of neutral as well as ionic radicals.[12] Attempts have been made by different groups[13-15] to develop good quality a-SiGe:H alloy films by the HeD technique. The optoelectronic properties of the material thus prepared were inferior to those prepared by the HD technique.[9,10] We believe that the possibility of producing device quality a-SiGe:H films has not yet been fully explored and needs further investigation.

In this article we report the results of our attempt to produce device quality a-SiGe:H films at high deposition rates by the HeD technique.

II. EXPERIMENTAL DETAILS

All the a-SiGe:H samples for this study have been prepared by rf plasma-enhanced chemical-vapor-deposition (PECVD) techniques (13.56 MHz) using a system supplied by Anelva, Inc., Japan. The details of the deposition system have been given elsewhere.[10] The alloy films have been prepared using SiH_4, GeH_4, and He (diluent) as feedstock (Matheson, U.S.A.). The details for the preparation of the films using H_2 as diluent are given in Ref. 10. The rf power density and chamber pressure were kept fixed at 60 mW/cm^2 and 0.8 Torr, respectively. The substrate temperature was kept fixed at 250 °C. Samples for the study of optoelectronic and IR vibrational spectroscopy were prepared on Corning 7059 glass and silicon wafer substrates, respectively. Schottky barrier structure solar cells were fabricated on stainless-steel substrates. A semitransparent palladium (Pd) film (100 Å) was deposited on the i layer by rf magnetron sputtering to form a metal-semiconductor junction.

For the measurement of mobility lifetime product $\eta\mu\tau$, monochromatic light of a wavelength corresponding to the absorption coefficient $\alpha \sim 10^3$ cm^{-1} of the material was chosen. The monochromatic light of proper wavelength was chosen by using an interference filter (Oriel, U.S.A.). All the $\eta\mu\tau$ measurements were done under same generation rate, i.e., 3×10^{18} cm^{-3} s^{-1}. Hydrogen bonding configurations have been analyzed by IR vibrational spectroscopy [Fourier transform infrared (FTIR), Perkin-Elmer 1710] and bonded hydrogen contents have been calculated by using the integrated area of the wagging vibrational modes at 630 and 570 cm^{-1}. The integrated oscillator strengths of Si—H and Ge—H bonds for wagging vibrational mode used in the calculation of bonded hydrogen content determination are 3.5 and 3 cm/mol bond, respectively.[16] For bulk defect density measurements, electron spin resonance (ESR) (RE1X, JEOL, Japan) has been used. The Urbach energy parameter E_0 of the alloy films has been determined by the constant photocurrent method (CPM). Internal quantum efficiency measurements using Schottky barrier structures were carried out under short-circuit conditions, using a lock-in amplifier (EG&G, Princeton Applied Research, 5210) and chopped monochromatic light.

III. RESULTS AND DISCUSSIONS

In Fig. 1 the deposition rates R_D of two types of alloy films, i.e., HD (curve 1) and HeD films (curve 2) are plotted
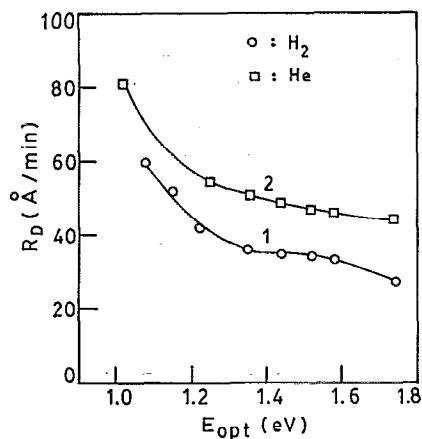
FIG. 1. Variation of deposition rate with optical gap of a-SiGe:H alloy films prepared under hydrogen (curve 1) and helium (curve 2) dilution.

against the optical band gap. It may be observed that at any optical gap R_D of the HeD films is higher than that of the HD alloys. The variation of dark conductivity σ_D and mobility lifetime product $\eta\mu\tau$ of HeD and HD materials is displayed in Fig. 2. Curves 1 and 1′ represent $\eta\mu\tau$ and σ_D of HD alloys, respectively, while curves 2 and 2′ correspond to those of HeD films, respectively. The error bars are introduced on each value of dark conductivity and mobility lifetime product in Fig. 2 so as to judge better the difference between the two growth conditions and their impact on the above two important photovoltaic parameters. It is observed that throughout the range of optical gap from 1.74 to 1.22 eV, $\eta\mu\tau$ of HeD alloys are higher than those of HD material. The difference between $\eta\mu\tau$ values of two types of samples increases with the decrease of optical gap; however, the σ_D of two types of films are same up to $E_{opt} \sim 1.4$ eV. For $E_{opt} < 1.4$ eV, σ_D of HeD films are higher than that of HD materials.
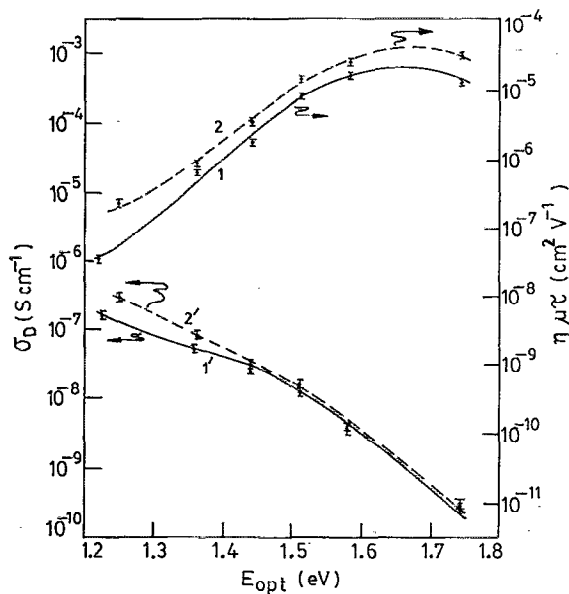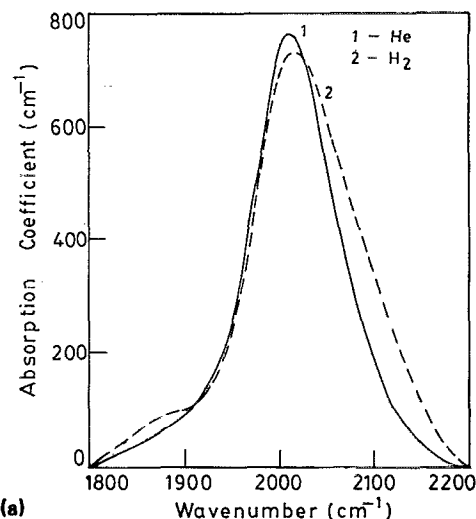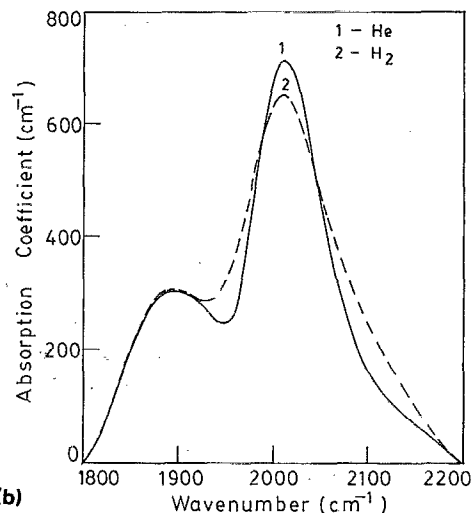

FIG. 2. Variations of mobility lifetime product $\eta\mu\tau$ and dark conductivity σ_D of HD and HeD films with optical gap.

FIG. 3. (a) Stretching vibrational modes in the IR spectra of HeD (curve 1) and HD (curve 2) films having an optical gap of 1.58 eV. (b) Stretching vibrational modes in the IR spectra of HeD (curve 1) and HD (curve 2) films having an optical gap of 1.36 eV.

In order to compare the structural properties of alloy films prepared with two different diluents (H_2, He) the Si–H stretching vibrational mode in the IR spectra of two typical HeD and HD films having optical band gaps of 1.58 and 1.36 eV are shown in Figs. 3(a) and 3(b), respectively. It may be observed from the figures that the values of the absorption coefficient due to polyhydride bonds (2080 cm^{-1}) are higher for films deposited under hydrogen dilution, i.e., helium dilution reduces the polyhydride bond formation. However, absorptions due to SiH (2000 cm^{-1}) and GeH (1880 cm^{-1}) bonds are nearly the same for two types of films in both the cases. In amorphous silicon and its alloys the ratio of polyhydride to the total bonded hydrogen is a measure of microstructure in the material.[17–19] So the decrease in polyhydride bonds due to helium dilution can be taken as an indication of improvement of microstructure. This is further supported by the fact that bonding modes of polyhydride bonds represented by 825, 845, and 880 cm^{-1} peaks have been reduced drastically in case of HeD films. Even for 2 μm film the
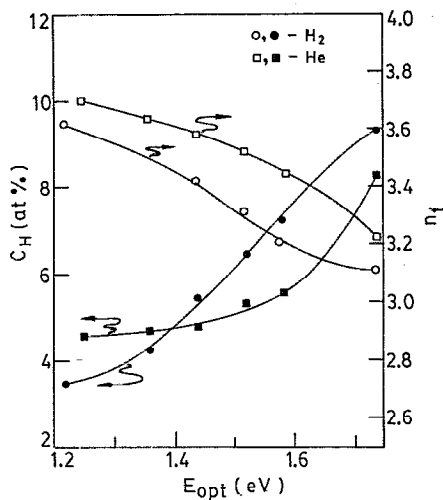
FIG. 4. Variations of bonded hydrogen content C_H and refractive indices n_f of HD and HeD films with optical gap.

Optical gap (eV)	Nature of dilution	Defect density (10^{16} cm^{-3} eV^{-1})	Urbach energy (meV)
1.58	H_2	3.1	47
	He	2.0	48
1.44	H_2	5.3	50
	He	6.0	51
1.36	H_2	9.0	60
	He	11.0	56

absorption due to the above-mentioned peaks is so small that it could not be detected while for HD films it could be easily measured.

Moreover, it has been observed in total IR spectra (400–4000 cm^{-1}) that with the use of helium dilution, the contamination level due to oxygen and carbon has been significantly reduced as is evident from the complete elimination of 780 and 1000 cm^{-1} peaks which represent oxygen- and carbon-related bonds, respectively.[20] This may enhance the stability of HeD films under prolonged illumination as proposed in the rehybridization two-sites (RTS) model of Redfield and Bube.[21] The variation of bonded hydrogen content C_H and refractive indices n_f with the optical gaps of HD and HeD films are shown in Fig. 4. It may be observed that the values of C_H are less for HeD films having $E_{opt} > 1.4$ eV compared to HD films; however, the reverse trend is noticed for low-band-gap materials. Moreover, the variation of C_H with E_{opt} is much less in case of HeD films than that of HD samples. Refractive indices of HeD films are found to be higher than those of HD films, particularly in the maximum alloying region which indicates that HeD materials are more compact with less microvoids than those of HD alloys. High refractive index, low bonded hydrogen content, and very low absorption due to $(SiH_2)_n$, and $(GeH_2)_n$ bonds confirm that the microstructural defect has been significantly reduced in cases of HeD films.

The values of midgap defect densities and Urbach energies of two types of samples at different bandgaps are shown in Table I. It may be noticed that N_D and E_0 values are either equal or slightly less for HeD films however, this small difference in defect densities of two types of films cannot account for the significantly higher $\eta\mu\tau$ values of HeD material as observed in Fig. 2. The improvement of $\eta\mu\tau$ values of HeD films may be attributed to the reduction of microstructural defects in the films due to the use of helium as diluent. Mahan et al.[17,18] and recently Jones et al.[19] have established an intimate correlation between degraded optoelectronic properties and increased heterogeneity associated with in-

creased microstructure. Moreover, the fact that simple structural modification of alloy films having similar midgap defect density can improve $\eta\mu\tau$ values has also been observed by MacKenzie et al.[22] In the low-band-gap ($E_{opt} < 1.45$ eV) region the position of the Fermi level with respect to conduction band is closer for HeD alloys compared to that for HD films. This also enhances $\eta\mu\tau$ values of HeD materials.

In order to study the hole transport properties in HeD materials (to judge their device potential), the internal quantum efficiency (QE) of four Schottky barrier (SB) solar cells based on HeD (curves 1 and 3) and HD (curves 2 and 4) intrinsic layers having 1.44 and 1.36 eV optical gaps are shown in Fig. 5. The uncertainty in the measurement of quantum efficiency has been calculated using the smallest unit of the measuring instruments. This is found to be nearly 4%. Thus, any change in QE greater than 4% between curves 1,2 and 3,4 may be attributed to the difference in the growth conditions of two intrinsic layers. The peak value of the QE curve for the HeD-material-based SB cell is higher than that of the HD-alloy-based device while the red response of both devices is nearly the same. Due to the nature of band bending in the S Barrier device, hole transport (lifetime and diffu-
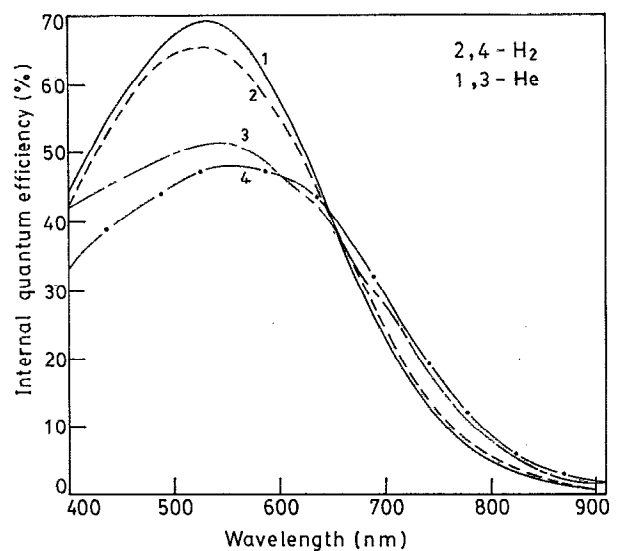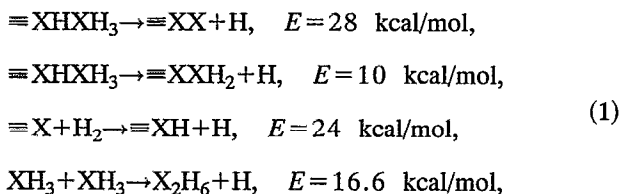

FIG. 5. Internal quantum efficiency of Schottky barrier solar cells with helium (curves 1 and 3) and hydrogen (curves 2 and 4) -diluted intrinsic layers and having same optical gap, 1.44 eV.

Middya, Hazra, and Ray

sion length) limits the carrier collection in the red/infrared part of the QE curve while electron transport does the same for the blue region.[23] Better blue response of HeD-based devices is consistent with the higher $\eta\mu\tau$ values of intrinsic layer. Higher peak values of curves 1 and 3 indicate that bulk recombination in HeD material is less than that of HD material which may be attributed to its reduction of microstructural defects. Nearly the same red response of two curves implies that hole transport properties of HeD and HD materials are nearly similar.

The results, described so far, can be correlated with the growth kinetics of alloy films. The energy of helium at metastable (He^*) and ionization (He^+) states is much higher (20 and 24 eV, respectively) compared to those of hydrogen atoms.[12] Under sufficiently high rf power density (60 mW/cm^2), large numbers of He^* and He^+ are generated. On deexcitation they transfer energy to electrons and ions within the chamber by collisions,[12]

$$He^* + e(\text{slow}) \rightarrow He(1S^1) + e(\text{fast}).$$
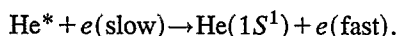
These fast electrons, energetic ions along with He^* by itself, increase the number density and kinetic energy of different species (SiH_3, GeH_3, SiH_2, and GeH_2, etc.) within the chamber. This leads to the enhancement of growth rate of HeD films compared to HD films. On the other hand, on deexcitation and neutralization of He^*, He^+, other ionic species (H^+, SiH_3^+, GeH_3^+) and radical recombination lots of electronic energy is transferred to the film growing surface as well as to the growth zone. Energy released at the growth zone initiates a series of exothermic reactions.[24] Consequently the "effective temperature" of the matrix increases. This leads to the enhancement of the surface mobility of adsorbed precursors, particularly heavy, sticky Ge-related radicals,[25] and helps them to find out the energetically favorable sites. Moreover, the thermally activated chemical reactions on the film growing surface, responsible for structural relaxation, are accelerated under He^*. This has also been observed by Shirai et al.[26] during "chemical annealing" treatment of a-Si:H and a-SiGe:H by He plasma. This leads to the formation of a rigid alloy network structure with low defect density. The experimental observations such as reduction of di/polyhydride bonds and bonded hydrogen content for alloy films deposited under helium dilution and having $E_{opt} > 1.40$ eV can be attributed to the fact that there are certain endothermic hydrogen-evolving surface reactions which can only take place under helium dilution. The reactions are written below:

$$\equiv XHXH_3 \rightarrow \equiv XX + H, \quad E = 28 \text{ kcal/mol,}$$

$$\equiv XHXH_3 \rightarrow \equiv XXH_2 + H, \quad E = 10 \text{ kcal/mol,}$$

$$\equiv X + H_2 \rightarrow \equiv XH + H, \quad E = 24 \text{ kcal/mol,} \quad (1)$$

$$XH_3 + XH_3 \rightarrow X_2H_6 + H, \quad E = 16.6 \text{ kcal/mol,}$$

where X=Si,Ge and the values of enthalpy E are for X=Si.[24] The consequence of these reactions are evolution of excess hydrogen by joining X—X bonds (X=Si,Ge). These reactions according to Robertson and Gallagher[24] fail to occur under HD silane and germane plasma since the hydrogen

atom is more tightly bound at the surface of the film than the energy supplied by the plasma to release the hydrogen atom/molecule from the surface. On the other hand, HeD silane and germane plasma under high rf power (60 mW/cm^2) may provide this requisite energy for hydrogen evolution from the surface. This explains the improved microstructure of HeD film compared to HD film.

IV. CONCLUSION

Device quality a-SiGe:H alloy films have been developed under helium dilution. Throughout the alloy region the mobility lifetime product as well as deposition rate are higher for HeD films compared to those for HD alloys although their defect densities are nearly the same. Improvements in electron and hole transport properties in HeD material are found to be consistent with the reduction of microstructural (macroscopic) defects. This work reveals a new result for the understanding of the growth mechanism of a-SiGe:H alloy using He dilution. This indicates that proper structural relaxation is the primary requirement to develop state-of-art alloy films that can be achieved in various ways such as hydrogen/helium dilution, reduction of deposition rate,[10] chemical annealing by atomic hydrogen,[21] or using fluorinated source gases.[6]

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J. Appl. Phys., Vol. 76, No. 11, 1 December 1994

Middya, Hazra, and Ray   7581

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